

KINETICS, CATALYSIS, AND REACTION ENGINEERING

Selectivity Studies of Oxygen and Chlorine Dioxide in the Pre-Delignification Stages of a Hardwood Pulp Bleaching Plant

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This work is concerned with the role of oxygen on the selectivity of chlorine dioxide in the pre-delignification stage of a *E. globulus* pulp bleaching plant. Its main purpose is to study the selectivity of chlorine dioxide when applied to an oxygen pre-delignified hardwood *kraft* pulp and to compare it to that of a conventional pre-delignification with chlorine dioxide (D). The intrinsic viscosity and kappa number were used to follow the polysaccharides degradation and the delignification rates. In an oxygen stage (O), the selectivity varies with the degree of delignification. In the initial fast phase of reaction it exhibits values similar to those of chlorine dioxide in a conventional pre-delignification stage (D), although it diminishes drastically in the second, slow phase of reaction. On the other hand, chlorine dioxide in a conventional pre-delignification stage (D) is a very selective agent and its selectivity remains practically constant along the process. Moreover, it's shown that it is independent of the initial viscosity and kappa number of pulp. However, when chlorine dioxide is applied to a previously oxygen delignified pulp, its selectivity decreases gradually with the extent of delignification in the preceding oxygen stage. The experiments suggest that the global selectivity of an OD sequence with *Eucalyptus globulus kraft* pulp can be improved if the delignification with oxygen is limited to the fast phase of reaction, which corresponds to the first 5–10 min of reaction.

Introduction

Environmental restrictions for bleach plant effluents and economic pressures have driven the pulp industry to implement new delignification and bleaching practices. In this context, oxygen delignification has emerged as an important processing technology. The benefits of introducing an oxygen delignification stage are substantial and include lower chemical requirements in subsequent bleaching sequences and higher brightness with equivalent amounts of bleaching chemicals. In addition, the use of oxygen delignification increases the total yield of the delignification stage, because it can be used to replace the final part of cooking which has a much lower selectivity. Furthermore, the liquid effluents from an oxygen delignification stage can be recycled to the chemical recovery system, thus reducing the environmental impact in the color, COD, BOD, and AOX of the bleach plant effluents. The main drawback of oxygen is the fact that lignin removal is limited to 50%, due to selectivity considerations, since beyond this level severe polysaccharide degradation occurs. As a result of this, a large number of research studies have pursued the improvement of oxygen selectivity in the pre-delignification stage. Several process modifications (two stage oxygen delignification systems), different pulp pretreatments (chelating agents, NaBH₄, NO₂, and acid wash-

ing), control of the main process variables (temperature, alkali charge, and oxygen pressure) and the use of different chemicals, employed as protectors (MgSO₄) or catalysts (polyoxometalates), have been reported in the literature as means of achieving this goal. On the other hand, the selectivity of chlorine dioxide has been scarcely investigated mainly due to previous industrial experiences, where the addition of small amounts of chlorine dioxide in the chlorination stage led to dramatic benefits on viscosity. One of the few works that addressed this subject was carried out by Teder and Tormund¹ who studied polysaccharide degradation in the first chlorine dioxide bleaching stage (D₁). They concluded that viscosity losses could be considered negligible in that stage and therefore the same could be expected in the delignification stage (D₀) since the content of lignin is much higher. Later, Rapson and Anderson² compared the performance of different oxidizing agents (hydrogen peroxide, peracetic acid, chlorine, and chlorine dioxide) with respect to brightness, viscosity, and color stability using only a single oxidizing chemical in all stages (xExEx) and found that only chlorine dioxide led to a pulp brightness above 90% ISO with an acceptable viscosity drop. Thus, due to its very selective behavior with unbleached *kraft* pulps and to the low selectivity of oxygen, the more extensive degradation of polysaccharides during an oxygen–chlorine dioxide (OD) sequence has always been imputed only to the action of oxygen. As a result, the selectivity of chlorine dioxide of oxygen pre-delignified pulps has

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never been investigated. The major objective of the present work is to study the behavior of chlorine dioxide, particularly of its selectivity, in the prebleaching stage of an oxygen pre-delignified *kraft* pulp from *Eucalyptus globulus*. The present study also provides useful information for determining the optimal oxygen delignification reaction time that prevents severe cellulose degradation during the OD sequence.

Methods and Materials

Kraft Pulping. The pulps used in this study were produced in the laboratory by *kraft* cooking of *Eucalyptus globulus* chips using the following operating conditions: effective alkali = 15.3% on o.d. wood, sulfidity = 30%, liquor-to-wood ratio = 8:1, initial temperature = 110 °C, and maximum temperature = 160 °C. The heating rate to reach the maximum temperature was of 1 °C/min. The time of cooking varied from 3 to 3.5 h (conventional cooking) to 6 h (extended cooking). The pulps were submitted to a set of consecutive washing cycles at 1% consistency with warm water (30 °C) and mechanically stirred for 30 min. At the end of each cycle, the pulp was centrifuged to about 25% consistency and fluffed by hand and a sample was taken for kappa number determination. This procedure was repeated until an asymptotic value of the kappa number was obtained, and this was considered the kappa number of the unbleached pulp. The remaining pulp was then stored in plastic bags and refrigerated at 4 °C for future use. All other analyses of the pulp were carried out after the full washing procedure.

Alkaline Oxygen Delignification. All the oxygen delignification experiments were carried out in a 1-L Parr reactor fully equipped for temperature and pressure control. To improve the gas–liquid–solid mass transfer, a special stirring device that maximizes the gas dispersion into the liquid–solid system, denominated “*gas entrainment impeller*”, was used. This is an impeller attached to a hollow stirring shaft, through which oxygen is continuously recirculated from the headspace above the liquid to the distribution ports located at the tips of the impeller. The driving force for gas recirculation is the vacuum at the tip of the impeller created by the rotation of the stirrer.

At the beginning of each run, 16.25 g o.d. of unbleached pulp and 650 mL of distilled water were fed into the reactor and the whole system purged with nitrogen for 1 min. Thereafter, the agitation was started and the reaction mixture heated to the desired temperature which took approximately 40 min. Once the pulp slurry reached the desired temperature (95 °C), a measured amount of alkali was introduced into the reactor using a small metal vessel pressurized with nitrogen. Immediately after this, the reactor was quickly pressurized with oxygen and the reaction time started. At the end of each run, the oxygen feeding line, the stirrer and the heating system were simultaneous turned off and the reactor depressurized to atmospheric pressure. The reaction vessel was then quickly opened and the pulp slurry transferred into a large volume of cold water to stop the reaction. The pulp was further washed with 3 L of warm distilled water (45 °C). In a preliminary set of trials, designed to establish the optimal conditions of alkaline oxygen delignification, the influence of oxygen partial pressure, reaction temperature, stirring rate, consistency, and reaction time were investigated. Several experiments were conducted over

Table 1. Standard Operating Conditions for the Alkaline Oxygen and Chlorine Dioxide Delignification Experiments

operating conditions	O stage	D stage
consistency, %	2.5	0.7
mixing speed, rpm	1050	600
temp, °C	95	55
chemical charge, % (on o.d. pulp)	1	3
oxygen pressure, barg	8	
reaction time, min	60	0–30

a large range of stirring rates (250–1550 rpm) and it was found that, above 650 rpm, mixing does not play any significant role on the delignification nor in the depolymerization rates of polysaccharides. Moreover, due to the strong dependence of the heat transfer on the stirring speed, it was observed that below 600 rpm it was very difficult to control the temperature effectively. To investigate if the agitation itself gives rise to physical fiber degradation, an experiment was conducted using only water in the liquid phase at 1100 rpm and a temperature of 110 °C for 60 min. The mean length of the fibers in both the original and the resulting pulps was measured using a *fiber quality analyzer* (FQA), and the results ($L_{\text{initial}} = 0.758$ mm and $L_{\text{final}} = 0.755$ mm) showed that this stirring device has no harmful mechanical action on the fibers. This experiment gives confidence that the degradation of polysaccharides measured at the end of each run will be solely a function of the chemical and physical processes taking place during the experiment. As part of this optimization strategy, some trials were also performed to determine the optimal consistency to be used in the experimental program: it was found that, up to 2.5%, the oxygen dispersion through the whole mixture was uniform and that the pulp properties, namely kappa number, CED viscosity, and ISO brightness exhibited a very satisfactory reproducibility. Therefore, on the bases of these preliminary studies and since the gas entrainment impeller operates best in the 800–1200 rpm range, the standard conditions used in subsequent experiments are those described in Table 1.

Chlorine Dioxide Delignification. The bleaching experiments with chlorine dioxide were carried out in a 2.6-L thermostatic glass reactor at low pulp consistency (0.7%), 3% chlorine dioxide charge, and at a stirring rate of 600 rpm (see Table 1); these values were established in previous experiments to ensure that delignification rate was not limited by mass transfer in the liquid film surrounding the fibers.³ After desintegration of the pulp suspension for 10 min, sulfuric acid is added just before chlorine dioxide, to impose the desired pH at the beginning of the reaction (pH = 4). The required amount of chlorine dioxide is added to the pulp suspension in approximately two seconds with a specially designed ampule pressurized with nitrogen and the time started immediately. The pH was kept constant throughout the experiment by successive additions of a sodium hydroxide solution and temperature was maintained by appropriate automatic control of a heating circulating fluid. In each experiment, liquid samples were taken with a syringe equipped with a glass filter and immediately analyzed after thermal conditioning. With regard to the pulp samples, rapid washing with a large volume of cold water stopped the reaction. The pulp was then further washed with an excess of warm water (35 °C) for kappa number, viscosity, and brightness determinations. Each run comprises a set of interrupted experiments where

Table 2. Quantification of the Repeatability and the Reproducibility of the Methods

method	mean	standard deviation (σ)
kappa/microkappa no.	5.14	0.03
CED viscosity, mL/g	1147	8
ISO brightness, %	75.70	0.14

chlorine dioxide concentration, kappa number, viscosity, and brightness were measured as functions of time, between 15 s and 30 min.

Chemical Characterization of the Pulp Samples.

The kappa/microkappa number, the intrinsic viscosity in copper(II) ethylenediamine (CED), and brightness were measured by the following methods, respectively: T236 cm-85, SCAN-CM 15:88, and ISO 3688-77. The main pulp used in this work had a kappa number of 14.6, a viscosity of 1427 mL/g, and a brightness of 41.6% ISO; the properties of the other pulps are indicated together with the discussion of results.

To quantify the repeatability and the reproducibility of the methods employed in our research lab where the chemical characterization of the pulp samples is made, an extensive group of experiments was conducted. The results obtained are indicated by means of the standard deviation and can be considered very satisfactory, as one can see in Table 2.

Discussion of Results

General. In the bleaching process, one of the most important objectives is to produce pulps with high strength properties and the required brightness. To achieve this, it is critical to ensure a high selectivity of the process, i.e., to minimize the relative rate of polysaccharides degradation with respect to the rate of delignification or brightening. In this context, selectivity, as defined above, can be expressed as a function of both the kappa number drop and the loss of viscosity:

$$S_i = \frac{1 - K_i/K_0}{1 - \eta_i/\eta_0} \quad (1)$$

where S_i is the selectivity at time t_i ; K_i , the kappa number at time t_i ; K_0 , the initial kappa number; η_i , the intrinsic viscosity at time t_i , mL/g; and η_0 , the initial intrinsic viscosity, mL/g.

In recent studies, some authors⁴⁻⁶ claim that the presence of hexenuronic acids strongly contributes to the kappa number determination. They also state that this influence is more relevant in the hardwoods than in the softwoods since the content of these acids is much higher in hardwood pulps. In the present work, this issue was not taken into account because the hexenuronic acid groups are unreactive in alkaline oxygen⁷ so their effect in the kappa number determination for every degree of delignification is always the same. Thus, although it is known that chlorine dioxide reacts with hexenuronic acids, the comparison of the selectivity of chlorine dioxide in the D and OD sequences using kappa number remains valid. In addition to this, a reliable quantitative method for the determination of hexenuronic acids content is not fully established, particularly in what refers to reproducibility.

Alkaline Oxygen Delignification. In a preliminary set of trials, we conducted a set of experiments to evaluate the separate role of oxygen and of sodium hydroxide. If only sodium hydroxide or oxygen are

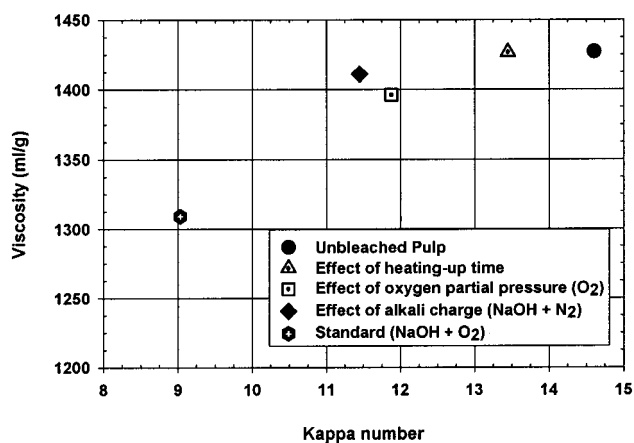


Figure 1. Individual effect of each variable in the oxygen delignification stage (operating conditions: temperature, 95 °C; alkali charge, 1%; oxygen partial pressure, 6 bar; reaction time, 30 min).

employed, a reduction of three kappa number units is observed, while if both are used simultaneously this value rose to five kappa number units, as one can see in Figure 1. This synergetic effect supports the hypothesis that phenolic groups are the major active sites in residual lignin and that its degradation proceeds through the phenolate anion that is produced by reaction of the hydroxide ion with phenolic components of lignin.⁸ In addition to these preliminary experiments, we carried out seven control runs where pulp was characterized just after the initial heating-up period. These revealed that the kappa number drops a single unit while the CED viscosity remains constant. The leaching of lignin from pulp fibers is a diffusion-controlled process and according to the diffusion theory, an increase in temperature should enhance the rate of leaching from the fiber wall.⁹ It is well-known that up to 70 °C there is an approximately proportional relation between the diffusion coefficient of lignin macromolecules and absolute temperature, although for higher temperatures this coefficient increases exponentially.¹⁰ When a fiber is in a liquid medium, the lignin macromolecules trapped inside the cell wall can diffuse to the outer bulk liquor or to the lumen. Furthermore, the dissolved lignin in the liquid retained in the lumen can diffuse directly to the outer bulk liquid through the large pits in the fibers wall. The diffusion of lignin trapped in the cell occurs in a time scale of hours while the lignin dissolved in the lumen diffuses during the first minutes, in the initial mixing phase.¹¹ This phenomenon might be the explanation for the kappa number drop during the initial heating-up period.

The most important issue in oxygen delignification is its selectivity, since it determines how far the delignification can proceed without a critical loss of pulp strength. In a set of eight experiments, the influence of temperature, oxygen pressure and alkali on the selectivity of the process was investigated for an *Eucalyptus globulus* pulp. The results are consistent with those reported in previous studies for different species.¹²⁻¹⁴ In Figure 2 one can see that the effect of oxygen pressure upon the selectivity is much lower than that of temperature. In the oxygen stage, both delignification and polysaccharide degradation proceed in two steps: an initial rapid phase of high selectivity followed by a slow nonselective residual phase^{13,15-17} as can be seen in Figure 3. This suggests that selectivity can be optimized by using high alkali and oxygen concentra-

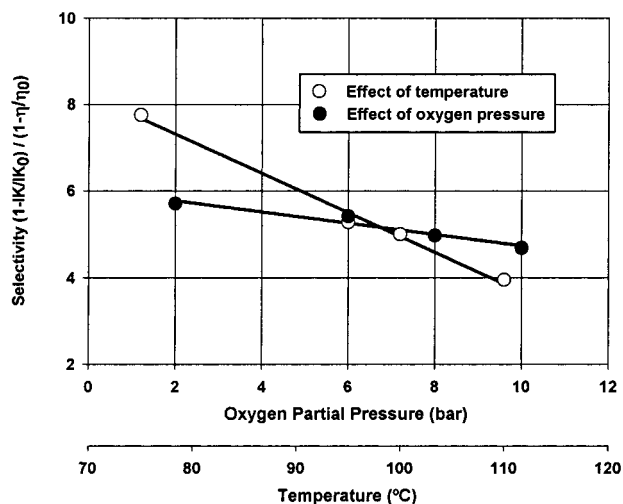


Figure 2. Effect of oxygen partial pressure (at temperature, 95 °C) and temperature (at oxygen partial pressure, 6 bar) in the selectivity of oxygen delignification stage (operating conditions: alkali charge, 1%; reaction time, 20 min).

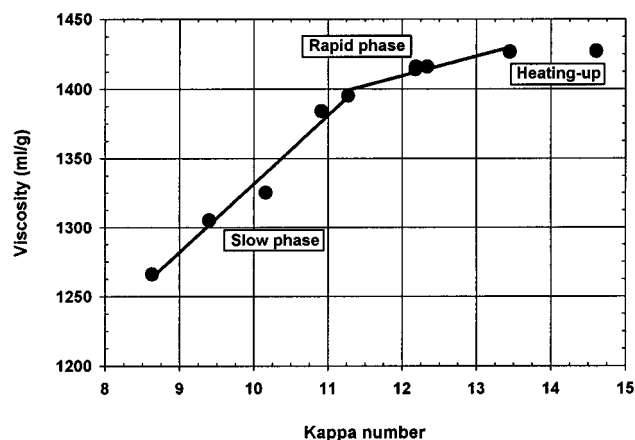


Figure 3. Selectivity of oxygen in the (O) pre-delignification stage (operating conditions: temperature, 95; alkali charge, 1%; oxygen pressure, 8 bar; reaction times, from 1 to 120 min).

tions in the initial phase and by reducing such concentrations in the last phase as has already suggested by other authors for softwood pulps.¹⁴

Chlorine Dioxide Delignification. The delignification of unbleached pulps with chlorine dioxide has been considered more selective than with any other bleaching agent such as chlorine, oxygen or ozone. It has been claimed that under standard industrial conditions chlorine dioxide should be completely inactive toward polysaccharides, and thus only few research efforts were dedicated to this subject. To clarify the effect of this reactant on the selectivity of unbleached hardwood pulps with different initial kappa numbers and viscosities, 26 bleaching experiments were carried at a constant temperature of 55 °C and a pH around 4, as illustrated in Figure 4. In this figure viscosity is plotted against kappa number after different reaction times, for unbleached *kraft* pulps with kappa numbers ranging from 11.0 to 14.6 and viscosities between 1250 and 1427 mL/g.

The overall degrees of delignification correspond to a reaction time of 30 min, except for the pulps with initial kappa numbers of 13.0 and 13.7, whose reaction times are 45 and 60 min, respectively. As expected, the degradation of polysaccharides in the D stage is very low when compared with the extent of delignification,

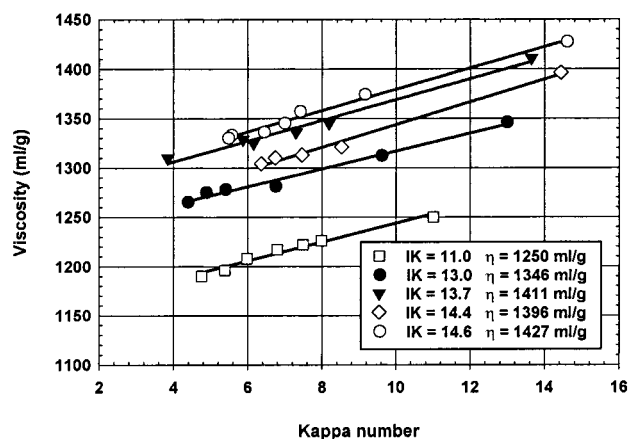


Figure 4. Selectivity of chlorine dioxide in the (D) pre-delignification stage (operating conditions: temperature, 55 °C; chlorine dioxide charge, 3%; reaction time, from 1 to 60 min).

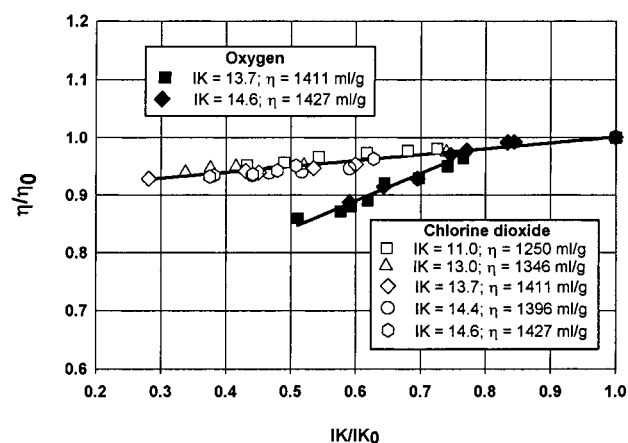


Figure 5. Normalized selectivities of oxygen in a O stage and of chlorine dioxide in a D stage.

independently of the initial values of kappa number and viscosity of the pulp. In addition to this, the reaction time has no effect on the selectivity of the process as can be seen for the pulps submitted to 45 and 60 min of reaction. If the data shown in Figure 4 is normalized with respect to the initial values of both variables, a global pattern is revealed for chlorine dioxide, which is shown by the upper straight line of Figure 5. As can be observed, even for pulps with very low initial lignin content (kappa no. = 11.0 and lignin content of 1.21%) the selectivity of the process is similar to that of the pulp with the highest kappa number (kappa no. = 14.6 and lignin content of 1.90%). This confirms the above considerations that chlorine dioxide is a very selective agent and, moreover, that its selectivity remains practically constant along the process. In contrast, the selectivity of oxygen is also independent of the initial kappa number but it is strongly related to the reaction phase of the process as highlighted by the lower straight line of Figure 5. In the initial phase of reaction the behavior is very similar to that of chlorine dioxide, but in the slow phase (i.e., after a period of around 5–10 min) it exhibits a severe decrease in selectivity.

Chlorine Dioxide Delignification after an Oxygen Stage: OD Sequence. As shown above, the delignification of unbleached hardwood pulps with chlorine dioxide is very selective, meaning that the rate of degradation of polysaccharides is low when compared with the rate of delignification. However, in view of the pressure on industry to introduce oxygen pre-delignifi-

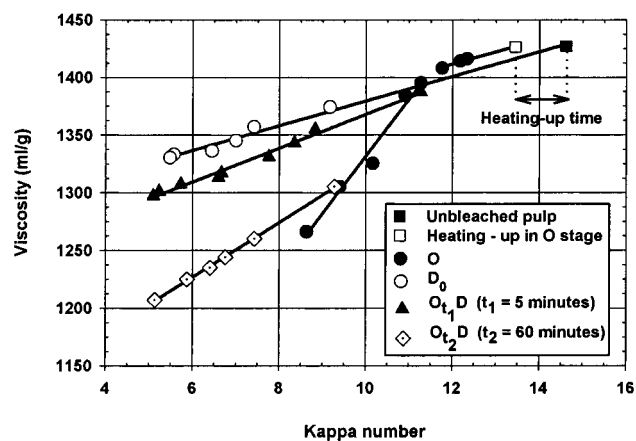


Figure 6. Comparison of the selectivity among oxygen delignification stage (O), first chlorine dioxide stage (D), and a chlorine dioxide stage after an oxygen stage (OD) (operating conditions in D stage: temperature, 55 °C; chlorine dioxide charge, 3%; maximum reaction time, 30 min. Operating conditions in O stage: temperature, 95 °C; alkali charge, 1%; oxygen partial pressure, 8 bar; maximum reaction time, 120 min).

cation systems, it is important to investigate if chlorine dioxide displays the same selective behavior when applied after an oxygen stage. Figure 6 illustrates the selectivities of four different processes: a complete oxygen stage (O), a chlorine dioxide stage applied to the same unbleached *kraft* pulp (D), and standard chlorine dioxide stages (OD) applied to pulps previously subjected to two different extents of oxygen delignification ($O_{t_1}D$ and $O_{t_2}D$). As referred above, the selectivity of oxygen in the first phase of reaction (5–10 min) is similar to that of chlorine dioxide in a D stage (slopes ≈ 11), whereas in the slow phase, the slope increases to 50, revealing a severe relative degradation of the polysaccharides. If the same unbleached *kraft* pulp is subjected to a conventional oxygen stage for 60 min and latter submitted to a D stage (OD sequence), the selectivity of chlorine dioxide is not the same as that seen in a single D stage when applied directly to an unbleached *kraft* pulp. In fact, the slope decreases from 24 ($O_{t_2}D$ sequence) to 11 (single D stage). The global selectivity of an OD sequence can be improved if the retention time in the oxygen stage is limited to the fast reaction phase ($O_{t_1}D$). In this case, the slope is reduced to values close to 15. This reduction of the reaction time in the oxygen stage enables the selectivity of chlorine dioxide in a OD sequence to approach that of a single D stage (applied to an unbleached *kraft* pulp) and thus, to maximize the overall selectivity of the sequence. In addition to this, since the extent of delignification of the $O_{t_1}D$ and $O_{t_2}D$ sequences is practically the same there are substantial savings in the total retention times when the first ($O_{t_1}D$) is the adopted strategy.

Figure 7 shows the normalized selectivity of chlorine dioxide when applied to two pulps with very low contents of lignin. One of the pulps was produced by the extended cooking described in Methods and Materials and the other by the conventional cooking followed by an oxygen stage, to obtain a kappa number near 11.0 in both cases and a viscosity of 1250 and 1387 mL/g, respectively. As can be observed by the slopes of the straight lines, the selectivity of chlorine dioxide is once again lower in the pulp previously delignified with oxygen. This is probably due to the differences in the lignin structure despite the same initial kappa number. It is well-known^{18,19} that oxygen attacks the type of

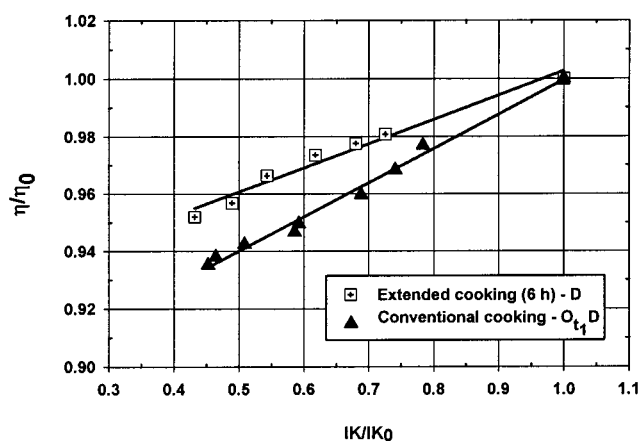


Figure 7. Effect of the delignification process in the selectivity of the D_0 stage.

lignin that is most reactive to chlorine dioxide and therefore the residual lignin after an oxygen stage is less prone to oxidation by chlorine dioxide. This might explain why the relative rate of polysaccharide degradation increases.

Conclusions

The selectivity of chlorine dioxide in a conventional pre-delignification D stage is independent of the initial kappa number and viscosity of the pulp. However, this pattern changes markedly when the pulp is previously subjected to a pre-delignification with oxygen. It was shown that the selectivity of chlorine dioxide, when applied to previously oxygen delignified pulps, decreases considerably with the extent of delignification in the oxygen stage. The results also reveal that the best global selectivity of an OD sequence can be achieved if the extent of delignification is limited to the initial fast reaction phase of oxygen, which corresponds to the first 5–10 min of reaction time. The attack of oxygen to the phenolic structures of lignin, very reactive to chlorine dioxide, and the modification of the structure of lignin along the reaction time could be the key to explain the increase in polysaccharides degradation rate as compared to the delignification rate.

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